Biomimetic Nano- and Micro-Structured Polymer/Inorganic Hybrid Materials by Using Self-Organized Honeycomb-Patterned Polymer Films

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論　文　内　容　要　旨

This doctoral theses described preparation of various novel biomimetic functional materials by combination with self-organized polymer structures as template or masks and inorganic materials, and also surface property measurements of these functional materials are discussed.

Chapter 1. Introduction

Recent years, biomimetics attract much attentions, and many biomimetic materials are created, such as mimicking superhydrophobic surfaces of lotus leave, anti-reflection properties of moth eyes, and so on. However, these materials are almost focused on only a specific function or a specific structure. In fact, surfaces in nature are more superior than conventional biomimetic materials. For example, some of insect eyes have multi-functions of anti-reflection and anti-fogging surface generated by surface nano-structures. Moreover, these functional surfaces are formed by low energy consumption processes of self-assembly and self-organization of protein and other biological materials. Thus, we should progress the biomimetics to mimic totally, which may lead to solutions of concern of our life, such as environmental problems and depletion of resources.

For adding functions to biomimetic materials, I focused inorganic materials, which is wisdom of mankind. Especially, nano- and micro-structured metal materials are widely used in electronic and photonic devices because of their large refractive indices, high thermal and electrical conductivities, and mechanical and chemical stability. The topology and dimensions of these materials are among the most significant factors in terms of their device applications.

In 1994, Francois et al. have reported preparations of self-organized honeycomb-patterned porous polymer films by using condensed water droplet arrays as templates. Honeycomb-patterned films have hexagonally arranged micropores, and also have characteristic double-layered structures connected with pillars located on apexes of honeycomb hexagons. When top layer of honeycomb-patterned films were peeled off, pincushion films with hexagonally arranged "spike" structures also can be obtained. And also microrings and microdots could be formed by thermal treatments of honeycomb-patterned films. Furthermore, honeycomb-patterned films can be used as templates for micro-lens arrays (MLAs), which are reflected structures of template water droplet arrays of

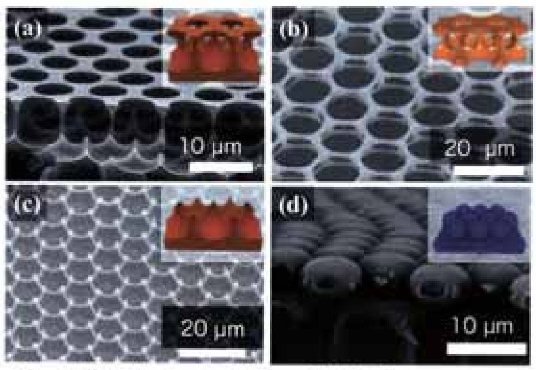

Figure 1 SEM images of self-organized polymer structures. (a) Honeycomb-patterned films, (b) Honeycomb-patterned films having penetrated micropores, (c) pincushion films and (d) micro-lens array, respectively

honeycomb-patterned films. In this way, various polymer nano- and micro-structures can be obtained by secondary processing of honeycomb-patterned films (Figure 1). In addition, these structures are prepared by self-organization process and simple secondary processing, so we can obtain these structures by mass productions of simple, easy, inexpensive and low consumption process.

According to the former mentioned backgrounds, this research aims to fabricate the novel biomimetic multi-functional surfaces by combination with polymer nano- and micro-structures prepared by low consumption process of self-organization and properties of functional inorganic materials. To achieve our object, various polymer-metal hybrid, metal and semiconductor nano- and micro-structures are fabricated by using honeycomb-patterned polymer porous films and their secondary processed structures as templates or masks.

Chapter 2. Preparation of the various nano- and micro-structures by using self-organized honeycomb templates

In chapter 2, we described preparations of various biomimetic functional polymer-metal hybrid and inorganic nano- and micro-structures by using self-organized polymer structured films as templates or masks and conventional metallizing methods or semiconductor processing (Figure 2). These structures have great potentials for various field based on the inorganic nano- and micro-structures. For example, silver is novel metal due to their specific properties including electro conductivity, surface plasmons, solid lubrication and so on. Therefore, various nano- and micro-structures covered by silver can be used for such as low friction surfaces (chapter 5), electroconductive films with limited view angle (chapter 6) and SERS substrates (chapter 7). And also silicon nano- and micro-structures can be used for superhydrophobic and superhydrophilic surface due to their large surface area (chapter 3 and 4). Especially, silicon nanospike-array structures can be also applicable for anti-reflection surfaces generated by gradually increased refractive index and optical well structures. Furthermore, not only the functions, one of the superior properties are their fabrication methods. To use of self-organized honeycomb-patterned polymer films as templates or masks, these functional structures can be obtained by large area, simple, easy and low consumption preparation method compared with conventional lithography based methods.

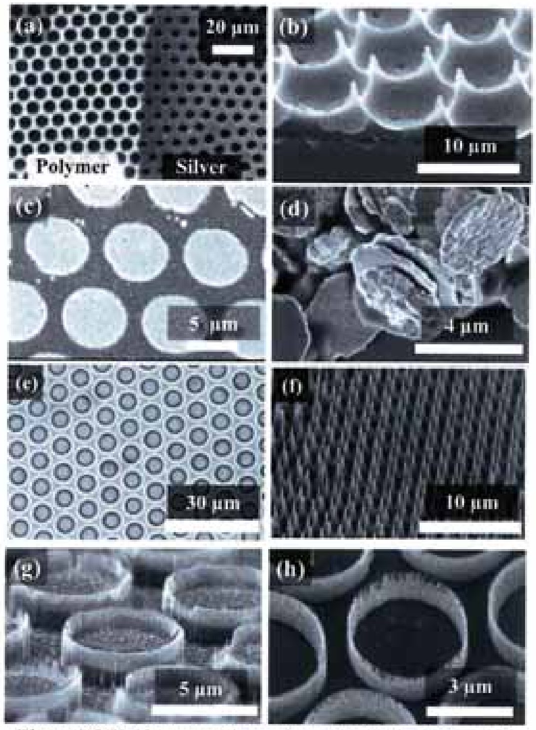

Figure 2 SEM images polymer/metal hybrid and inorganic nano- and micro-structures. (a) metallized Honeycomb-patterned films, (b) metallized pincushion films, (c) silver microdot arrays, (d) silver microdisks, (e) silicon micro-hole arrays, (f) silicon nanospike arrays, (g) silicon microdots and microring arrays, (h) silicon microring arrays, respectively

Chapter 3. Applications for anti-reflection and superhydrophobic surface

In nature, there are many functional surfaces generated by nanospike-arrays, including a moth eye and a lotus leaf. In chapter 2, I described preparation of silicon nanospike-array structures by dry etching with self-organized 3-dimensional porous polymer masks, which may show functions generated by nanospike-arrays. Therefore, in this chapter, properties of silicon nanospike-arrays were measured.

As results of surface properties measurements, silicon nanospike-arrays show anti-reflection property generated by hierarchical nanospike structures, such as moth eye structures and optical-well structures (Figure 3). This silicon nano-structures also have superhydrophobic property realized by large surface area and surface fluorocarbons, which formed during etching process (Figure 3, inset image). This biomimetic bi-functional silicon

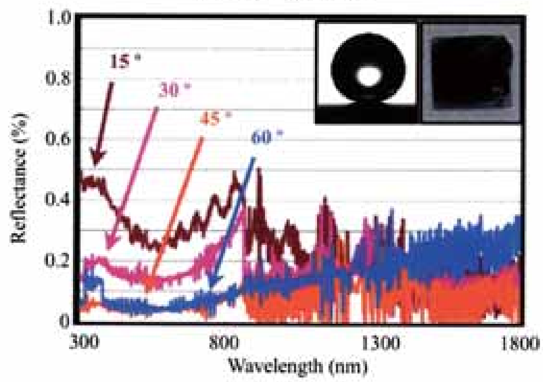

Figure 3 Reflection spectra of the silicon nanospike-array structures. Inset images show photographs of water droplet on silicon nanospike-array structures and apparatus of silicon nanospike array-structures

nanospike-arrays have large surface areas compared to "black silicon", so it is suitable for various practical applications, including high efficiency solar cells.

Chapter 4. Applications for wettability and structural patterned surfaces

I deeply focused surface wettability because there are various excellent water controlling surface in nature. Simplest water controlling surfaces in nature is superhydrophobic surfaces of a lotus leaf. A lotus leaf uses their surface water repellency property for surface self-cleaning. Next generation of water controlling surfaces is a rose petal, which surface shows superhydrophobic, but high water adhesion properties for moisture retention. Moreover, some beetles in desert collect drinking water from fog-laden wind on their back, which is patterned by superhydrophobic and hydrophilic surfaces. As these facts suggested that patterning of wettability or structures have great potentials for controlling water.

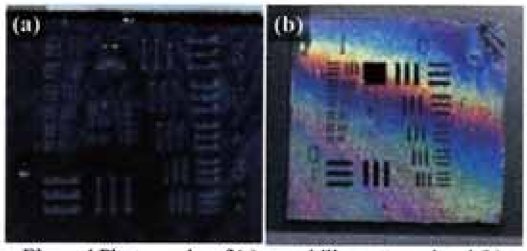

Figure 4 Photographs of (a) wettability patterned and (b) structural patterned silicon nanospike-array structures.

In the previous chapter, we showed the surface properties of a biomimetic bi-functional silicon nanospike-array structures. And their surface property of superhydrophobicity was generated by large surface area and surface fluorocarbons. So, when surface fluorocarbons are eliminated, their surface wettability was dramatically changed to superhydrophilicity. By UV-O_3 treatment with photo-masks, wettability patterned silicon nanospike-arrays were obtained (Figure 4(a)). And also patterning of silicon nanospike-array structures were achieved by patterning the porous polymer masks (Figure 4(b)). These structural patterned surfaces also show wettability differences between flat and structured surfaces. These results suggest, arbitrarily 3 different wettability patterned surfaces can be obtained by combination with surface chemistry and structural patterning by UV-O_3 treatment with photo-masks. These functional surfaces can be applicable for wide variety of fields, such as water transport devices, water manipulated surfaces, water fluidic devices and so on.

Chapter 5. Applications for low frictional surface

Friction is one of the important factors in various fields, so controlling the surface friction is strongly expected. For examples, if very low friction surfaces can be prepared, problems including loss of mechanical energy by thermal energy radiation and abrading parts are solved, and it becomes reduction of environmental burdens. In nature, some snakes and insects control surface frictions by surface nano- and micro-structures. So, nano- and micro-structures have possibilities for controlling surface frictions.

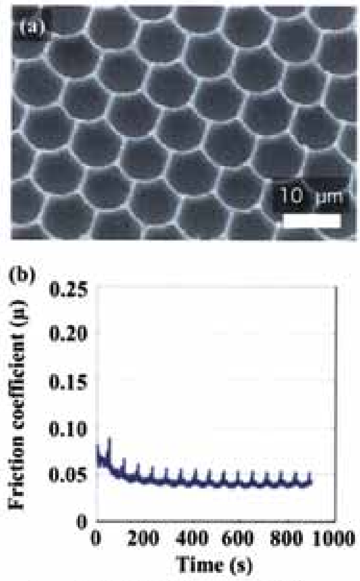

Figure 5 (a) A SEM image of silver deposited microdimple-structured films. (b) A graph of friction coefficient.

Because it is known that silver acts as solid lubricant, I measured surface friction coefficients of silver coated microdimple-structured films. As results of friction coefficients measurements, the silver coated microdimple-structured films showed quite low friction coefficients, and 8 μm period film has lowest friction coefficients (Figure 5). This low friction surface may generated by their micro-structures and solid lubricant of surface silver. These results suggest that silver coated microdimple-structured films can be applicable to low frictional surfaces.

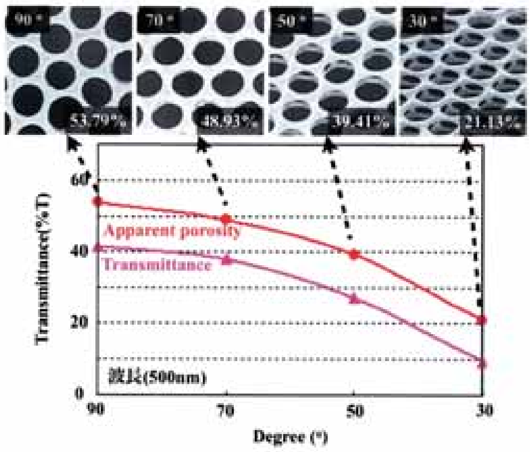

Figure 6 Tilted SEM images of honeycomb-patterned films and transmittance spectra.

Chapter 6. Applications for electroconductive films with limited view angles

Recent years, transparent and electroconductive films are very important materials for transparent electrodes in flat panel displays, thin film solar cells and so on. At present, indium tin oxide (ITO) films with a low resistivity and with stable electrical, optical and mechanical properties for practical applications are generally used. However, ITO is a relatively expensive materials because indium is not abundant. So, alternative materials of ITO are demanded.

The metallized honeycomb-patterned films having penetrated micropores have potentials for transparent electroconductive films because of their porosity, and also the films have additional properties based on their double layer structures. In this chapter, the unique optical properties of these metallized honeycomb-patterned films having penetrated micropores were shown. As results of transmittance spectra, metallized honeycomb-patterned films show limited viewing angle property, which are generated by double layer structures of honeycomb-patterned films (Figure 6).

Chapter 7. Applications for SERS substrates

Metal nano-structures, especially gold and silver, attract much attentions due to their unique surface plasmon resonance (SPR), which enhances electromagnetic fields at the surface of metal nano-structures. By using high electromagnetic fields of SPR, metallic nano-structures have proven to be good candidates for applications in catalysis, biosensors, plasmonics and surface enhanced Raman scattering (SERS), of which chemical and biological sensing are the most promising. Especially, SERS are very attractive applications because Raman scatterings from single molecule can be detected by using SERS substrates. Since SPR strongly depends on their specific composition, size, local dielectric environment and electromagnetic interactions with nano-structures, shapes of nano-structures are very important. There are two important structural factors for enhancing electromagnetic fields; one is a metal sharp edge (edge-mode excitation), the other is metal nanogaps (gap-mode excitation).

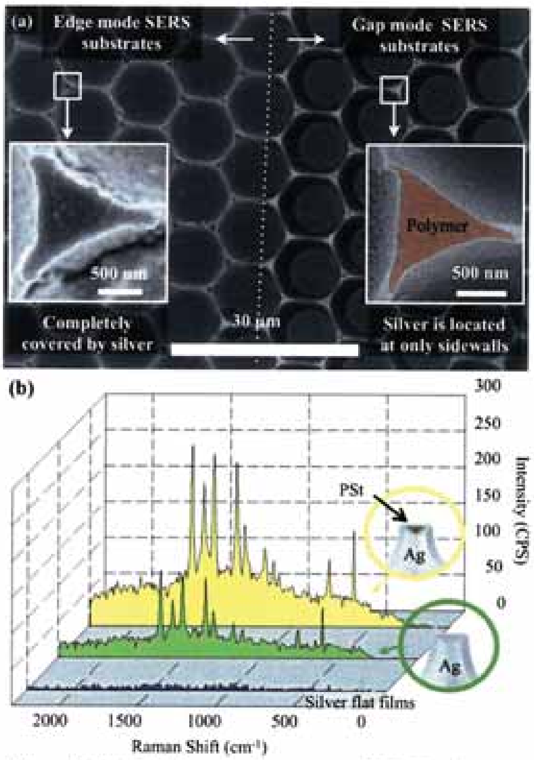

Figure 7 (a) A SEM image of two types of SERS substrates.
(b) SERS spectra by using the prepared substrates.

In this chapter, we show preparation of SERS substrates focused on above two structural factors by self-organization and vapor deposition processes (Figure 7(a)), and measurements of SERS of rhodamine 6G (R6G) aqueous solutions on them. As results of Raman scattering measurements, it is suggested that silver deposited pincushion films and the arrays of triangular polymer spike with silver nanowalls enhance Raman scattering (Figure 7(b)). Especially, the arrays of triangular polymer spike with silver nanowalls strongly enhanced Raman scattering from dilute solutions of R6G with quite low laser intensity. Comparing Raman scattering enhancements of the both cases, the arrays of triangular polymer spike with silver nanowalls may enhance Raman scattering by combination with "edge-mode" and "gap-mode" structural factors. These arrays have great potentials for practical use because of template flexible polymer structures and potentials for large area fabrications. Furthermore, in addition to their use as SERS substrates, the films can be applied to a wide variety of functional materials for plasmonic devices.

Chapter 8. Conclusions

In this thesis, we suggest next generation of biomimetics, which are not only mimicking a function, mimicking appropriate multi-functions and also low energy formation processes. Therefore, functional materials prepared in this thesis have great advantages for practical use compared with preparation methods of conventional lithography based technology. Furthermore, these functional materials are just only the one of examples based on biomimetics. Because various periodic patterns can be formed by self-assembly and self-organization process, and also undiscovered excellent functions are surely still existed in nature. It is believed that this research contributes developments of material science and nanotechnology as well as biomimetics.

論文審査結果の要旨

本論文の目的は、生物の表面が有する微細構造とそれによる機能発現を材料設計指針とし、自己組織化プロセスにより作製されるハニカム状高分子多孔質膜を出発材料として、高分子/無機ハイブリッドや半導体、金属を作製するものである。

第1章は、序論であり、研究の背景となる生物模倣技術と自己組織化による高分子多孔質膜作製について述べている。

第2章では、ハニカム状多孔質膜を用いた有機・無機微細構造体の作製法について述べている。高分子微細構造を鋳型としたハイブリッド微細構造の作製、高分子微細構造をマスクとしたシリコン微細構造の作製に成功している。

第3章では、超撥水・無反射表面への応用について述べている。ハニカム状高分子膜を加工して得られたピラー構造を有する多孔質膜をドライエッチングのマスクとすることで、シリコン表面に規則的なナノスパイクアレイを導入した。この表面が、モスアイ構造と呼ばれる無反射特性とロータス効果として知られている超撥水性を持つことを明らかにした。

第4章では、濡れ性のパターニングとその応用について述べている。超撥水性シリコン表面をフォトマスク下でUV-オゾン処理することで、超親水性と超撥水性のパターニングができた。表面張力差を駆動力とする水滴輸送デバイスの原理確認をした。

第5章では、低摩擦表面作製について述べている。蛇や昆虫は、体表面の微細構造により摩擦低減や制御を行う。ハニカム状多孔質膜を出発材料として銀の微細構造を作製した。構造化された銀表面は平滑面よりも低い摩擦係数を示した。

第6章では、視野角制限フィルムの作製について述べている。ハニカム状多孔質膜は2層構造を有しており透過光の入射角依存性が大きい。メッキをすることで角度依存性を保持したままで光透過率が増加する現象を見いだした。

第7章では、金属構造体の表面増強ラマン散乱基板への応用について述べている。ピラー構造を有する高分子膜に銀を蒸着して微細な金属間隙を作製したところ、ラマン散乱が増強されることを明らかにした。

第8章は本論文の総括である。

以上、本論文は、生物模倣による機能デザインに基づき、自己組織化技術を駆使することで、表面微細構造を特徴とする無機材料や高分子・無機ハイブリッド材料を作製した。これは材料科学の発展に大きく寄与するものである。

よって、本論文は博士（工学）の学位論文として合格と認める。